Remarks/Arguments:

This is a reply to the final rejection of June 18.

We request the examiner reconsider the prior art rejections in the final rejection, for reasons expressed below.

a) Formalities

Claim 23 has been corrected to read "Compound Parabolic Concentrator (CPC)" (not "reflector").

b) Wide-angle illumination and Compound Parabolic concentrators

We believe there is some confusion about the terms "wide-angle illumination" and "Compound Parabolic Concentrator (CPC)". Therefore, a detailed explanation of those terms is given.

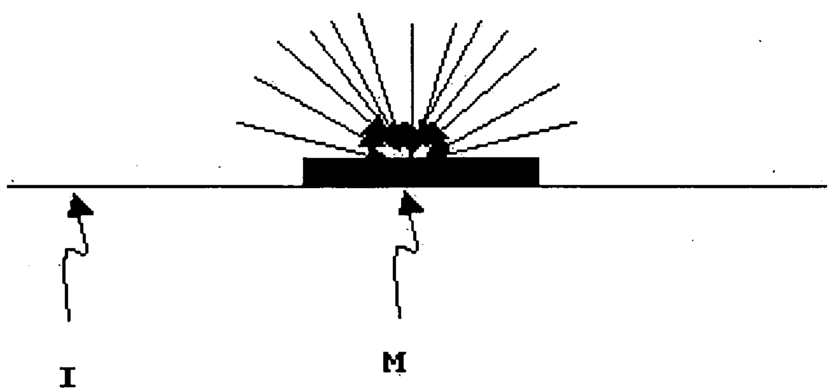
The present specification contains a clear definition of the term "wide-angle illumination". On p. 6, end of first paragraph, it states that

> "wide-angle illumination optics are capable of illuminating the marking simultaneously under a plurality of incidence angles ranging from orthogonal to grazing incidence."

Please note that the word "Preferably" has only been added here since the indicated incidence angles are preferred. Basically, wide-angle illumination means simultaneous illumination of a marking under a plurality of incidence angles.

This is also expressed in the passage of the present specification on p. 6-7, bridging para: "The OVD receives thus light of sequentially changing color simultaneously under all incidence angles, i.e. from substantially orthogonal to substantially grazing incidence."

The following drawing (which was not in the original specification) illustrates wide-angle illumination as defined above:

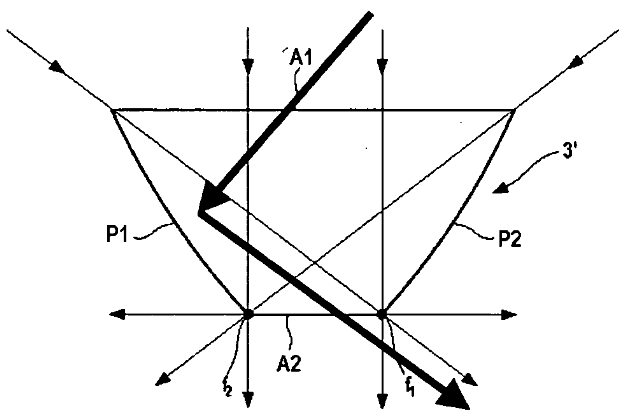


A marking (M), which is located on an item (I), is simultaneously illuminated under a plurality of angles. As one can see above, the angles on incidence under which the marking (M) is simultaneously illuminated may vary from 90° (orthogonal) up to an incidence angle slightly above the surface plane of the item (I), the so-called grazing angle.

What is the purpose of wide-angle illumination? It is well known that various optical security features such as holograms or optically variable pigments only reveal their optical characteristics when they are illuminated under different angles of incidence. Optically variable pigments, for example, have to be observed under different angles, the grazing angle and the face angle (see the enclosed article by Schmid et al., Fig. 6).

The angles under which a certain security element has to be simultaneously illuminated differ from security element to security element. This is why conventional authentication devices are only capable of detecting one specific security element: Conventional authentication devices may only illuminate security elements under one or at most very few fixed angles of incidence.

The present invention provides a solution to the problem that for different security elements different authentication devices have to be used. The present invention provides an authentication device which exploits the above concept of wide-angle illumination and thus simultaneously illuminates a marking under a plurality of angles of incidence. The device is shown in Fig.1 of the specification:



An item (I) comprises a marking (M), as already shown above. The authentication device comprises a Compound Parabolic concentrator (CPC, reference number 3). Said CPC is described in detail in the original specification, p. 7-8:

> "A Compound Parabolic Concentrator (CPC) is characterized by a longitudinal section which is delimited by two parabolic elements (P1, P2; Fig. 1c), having parallel axes and being arranged such that said parabolic elements' focal points (f1,

f2) lie each on the respective other parabolic element. The CPC can be made in the form of a 2-dimensional slab or in the form of a 3-dimensional cone (rotational body). It can further be made either as an internally reflecting hollow body, or as a solid dielectric body, which latter may further carry a reflecting coating or a mirror on part of its outer surface.

"The CPC has a first (A1) and a second (A2) aperture area, and a first and a second acceptance angle for incoming or outgoing light, whereby said first aperture area is wide and has a narrow acceptance angle, and said second aperture area is narrow and has a wide acceptance angle. Light falling into the first aperture area of the CPC within its acceptance angle is emitted from the second aperture area of the CPC within its acceptance angle, and vice-versa.

"The incoming light to the CPC is furthermore scrambled, such that a single light source, located anywhere in front of said first aperture area of the CPC, will illuminate the whole second aperture area of the CPC under all angles which are comprised within its acceptance angle. A CPC, and more generally any other suitable non-imaging optics device, can thus be advantageously used to convert the emission of a plurality of LEDs located in front of its first, larger aperture area to a hemispherical diffuse illumination of the sample located in front of its second, smaller aperture area."

The CPC is illustrated in Fig. 1c of the specification:

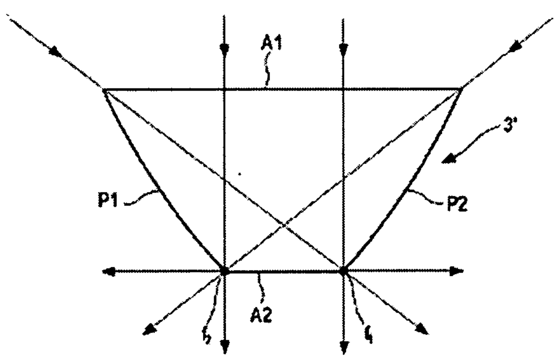
The following things are very important:

- A CPC is a specific optical device characterized by a specific arrangement of two parabolic elements (P1, P2).

- The light source or light sources are located above the first, wide aperture area (A1) of the CPC . This is clearly shown in Fig. 1a (and in Fig. 1b as well), and also expressed on p. 8, second and third para.

- The marking to be illuminated is located below the second, narrow aperture area (A2) of the CPC.

Fig. 1c



- Within the CPC, the incoming light is scrambled so that even with one light source it is possible to illuminate the whole second aperture area, i.e. wide-angle illumination is achieved. In other words, light coming in from the wide aperture area (A1) is reflected at the inner surface of one of the parabolic elements (P1, P2) and will leave the CPC through the second narrow aperture area (A2). For example, a thick light beam will be reflected like so:

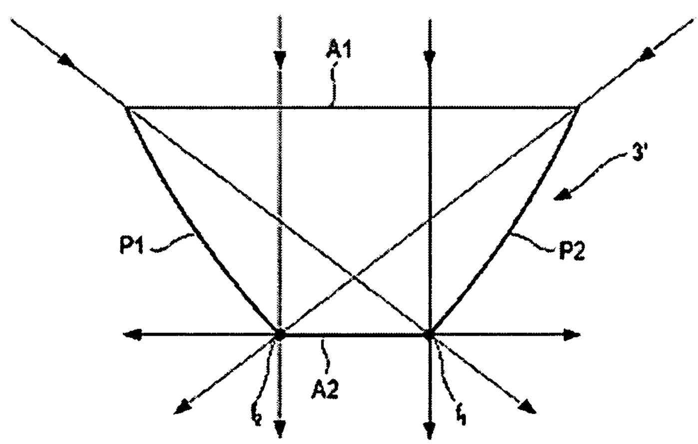
This will occur with a plurality of light beams (which enter under different angles and will thus be reflected under different angles) and result in the desired wide-angle illumination.

It is respectfully submitted that this concept is neither shown nor suggested in the cited prior art.

c) Alcock does not teach wide-angle illumination or a CPC

On p. 3, end of first para, of the office action, the examiner states:

"wherein the illumination of steps a) and d) is wide-angle illumination (see pg. 2 L:



18-25 Since there are more than one light sources they must be at different positions, therefore there would be a wide-angle illumination)."

First of all, the passage in Alcock (pg. 2 L: 18-25) referred to by the examiner states:

"According to a first aspect of the present invention a method of detecting the presence of a non-pearlescent OVM in or on a surface, comprises the steps of illuminating the surface at a first angle to the surface and detecting and determining the frequency spectrum of scattered light in two different directions from the surface, one direction subtending an angle to the surface which is substantial different from the said first angle and is substantially parallel to the plane of the surface, and the other direction subtending an angle to the surface which is substantially closer to the said first angle than the said one direction."

In said passage, only illumination at a first angle is mentioned (underlined by the applicant). It is not stated at all that there would be different light sources at different locations. The scattered light is detected in two different directions. However, detection is carried out using detectors, not light sources.

It is respectfully submitted that the passage in Alcock referred to by the examiner does not give any teaching of wide-angle illumination at all. To the contrary, it teaches illumination under one angle (the first angle).

Applicant has furthermore reviewed the remaining disclosure of Alcock and could nowhere find any sign of wide-angle illumination. Alcock uses only one light source without an optical means such as a CPC. One light source alone is of course not capable of providing wide-angle illumination.

There is a reference in Alcock to the use of light of two different wavelengths:

> "In a method incorporating the said third aspect of the invention, the surface may be illuminated by the two monochromatic components simultaneously, or preferably separately first with monochromatic light of one wavelength $\lambda 1$ and then with monochromatic light of the second wavelength $\lambda 2$."(p. 5, 2nd para)

However, this does not refer to wide-angle illumination. First of all, even the use of two light sources (which are not even described) would, without any such optical means as a CPC, not result in the above-described wide-angle illumination. Secondly, Alcock teaches that the two light beams of different wavelengths are arranged along one common projection axis:

> "According to the invention there is provided apparatus by which an output signal is generated indicative of the presence of a specific OVM in or on a surface under test comprising:
> 1. A light source which produces and projects along a projection axis monochromatic light at each of two wavelengths λ1 and λ2 selected according to the specific OVM of interest" (p. 8, l. 10-15)
>
> "It is preferable for the light source to comprise a pair of LED's, one which emits near monochromatic light at or near λ1 and the other at or near λ2, and the light from the two LED's is projected along a common axis." (p. 9, l. 12-14)
>
> "According to a sixth aspect of the invention a further method of identifying the presence of a particular type of material on a printed or coated surface, comprises the steps of:
> 1. Illuminating the surface at a pre-set angle to the surface with substantially monochromatic light at three wavelengths λ1, λ2 and λ3 selected in accordance with the particular type of material,

In other words, there is provided one light source comprising a pair of LEDs which emit light of different wavelengths at one common axis. Thus, the emitted light of different wavelengths proceeds in parallel to each other.

This is shown in Fig. 1 of Alcock:

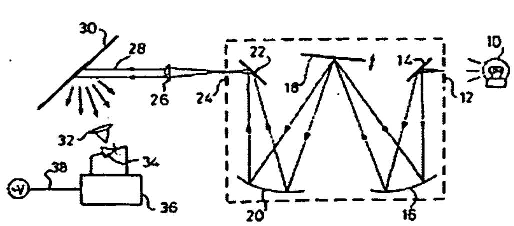


Fig. 1

It is evident that a <u>parallel</u> beam of light 28 is projected onto the sample 30 (see also p. 26, . l. 16-18).

In Fig. 6, it is shown that two LEDs (80, 82) are comprised at the same location within one light source. In said figure, the parallel beams of light are even conveniently only shown as one light beam (see also p. 30, last para):

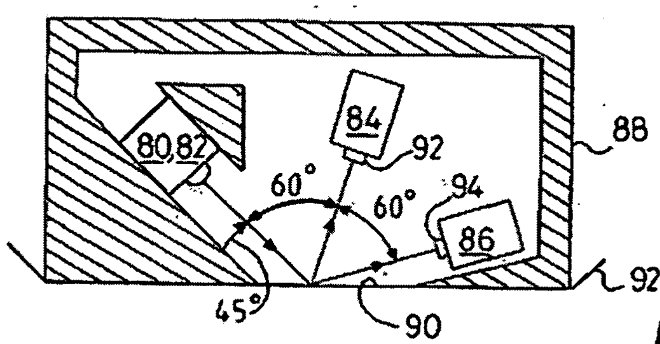


Fig. 6

In summary:

- Alcock does by no means teach or suggest wide-angle illumination.
- Alcock does nowhere teach or suggest a Compound Parabolic Concentrator (CPC).
- Alcock uses one light source. Said light source may comprise two (or three) LEDs emitting light of different wavelengths. However, in said embodiment the emitted light beams proceed parallel to each other, hitting the sample under the same one angle of incidence.

Applicant therefore believes that Alcock is not a pertinent reference against the present invention.

Should the examiner nevertheless remain of the opinion that Alcock would disclose wide-angle illumination or a CPC, it is respectfully requested that the examiner

a) explains where in Alcock he believes to have found a respective teaching

b) comments on the above cited passages from Alcock.

d) Plesko does not teach wide-angle illumination

In the outstanding office action, the examiner has newly cited Plesko (US-5,932,860) against the present invention.

It is correct that in Plesko a Compound Paraobolic Concentrator is mentioned (col. 17, lines 16-21, 34-56).

However, Plesko does not use the CPC for wide-angle illumination of a security marking.

Plesko teaches a hand-held bar-code scanner, as shown in Fig. 1 of Plesko. From the tip of the hand-held scanner, light is emitted to fall onto the bar-code. The scanner is moved along the bar-code, and light reflected from said bar-code is collected by the tip of the hand-held scanner (Fig. 1, col. 15, l. 56, to col. 16, l. 22).

Within said hand-held scanner, a scan-module for receiving the incident light from the bar-code is comprised. The scan module of interest, i.e. the one comprising a CPC, is shown in Figs. 6 and 7 of Plesko. In Fig. 7, it is designated as 16 and described as follows:

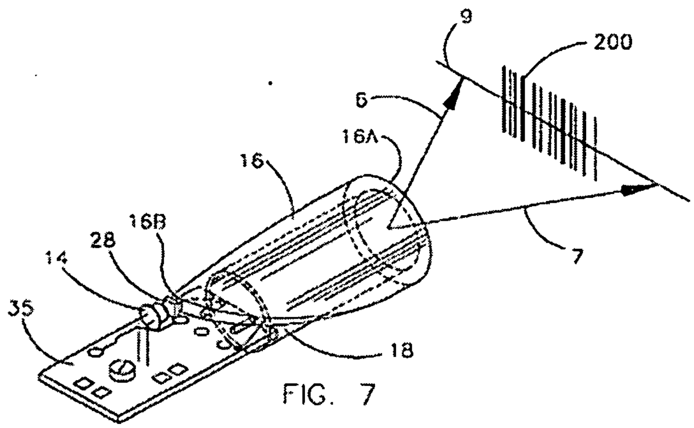


FIG. 7

"Now turning to FIG. 7, a further addition is made to the inline scan module of FIG. 8, namely a non-imaging coaxial light concentrator 16. The non-imaging coaxial light concentrator 16 has been described in another Patent Application for an Electro-Optical Scanning System with Gyrating Scan Head, Ser. No. 07/776,663, filed by the same applicant. The non-imaging light collector functions by accepting light returned from a scanned target at its front end 16A, and concentrating the light by means of internal reflection to small exit area 16B, where the concentrated light is directed upon photo electric converter 14."

Here, the CPC is not used as a means for wide-angle illumination. Rather, it is not used for illuminating the bar-code at all. To the contrary, the CPC accepts light reflected from the bar-code by its wide front end 16A, and releases it onto a photodetector through its small exit area 16B.

In other words, Plesko uses the CPC only for its main purpose, i.e. for concentrating light from a target onto a detector. In this respect, the reflected light enters the CPC through its wide aperture area, and leaves the CPC though its small aperture area.

This is in complete contrast to how the CPC is used according to the present invention. As described above with respect to Figs. 1a and 1c of the present specification, according to the present invention the CPC receives light from the light source (not reflected light from the security marking) through its wide aperture area. Said light leaves the CPC through its small aperture area and subsequently hits the security marking under a plurality of angles of incidence.

Also in Fig. 6 of Plesko, the CPC (here designated as 34, see col. 17, l. 38-43) is used in an opposite was as compared to the present invention. Plesko states here:

"Light concentrator 34 may be a positive condenser lens but in a preferred embodiment of the present invention it is a non-imaging light concentrator, namely a compound parabolic concentrator made from a transparent solid dielectric such as plastic, which concentrates light by internal reflection upon a photo diode 14."
(Col. 17, l. 38-43).

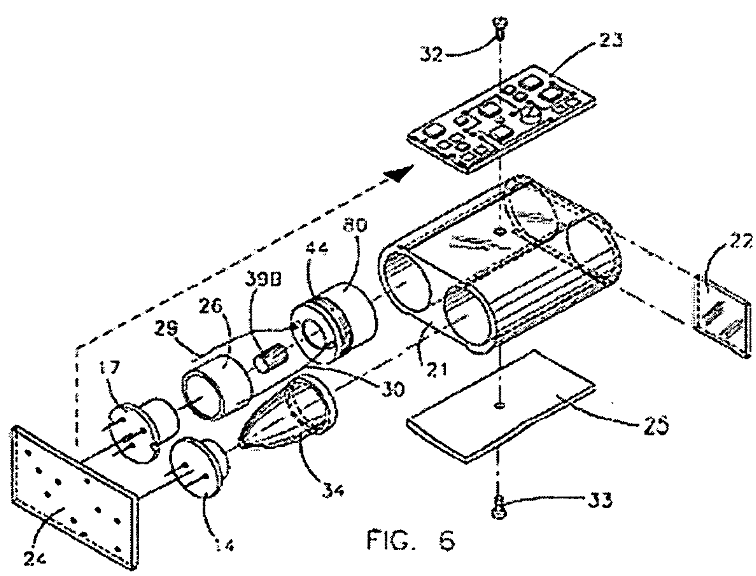


FIG. 6

Also here, the small aperture area of the CPC 34 undoubtedly points into the direction of the photodetector 14.

In summary:

- Plesko describes the use of a CPC. However, the CPC is used in complete opposite as compared to how it is used in the present invention. In Plesko, the CPC is used in the detection part of a hand-held scanner. The CPC receives the light reflected from the security marking and concentrates it onto a detector unit. The CPC is used for concentrating reflected light.
- In contrast thereto, in the present invention the CPC is used in the illuminating part of the authentication de-vice. There, the CPC serves to distribute the light from a light source such that it hits upon the security marking under a plurality of angles. The CPC is used for wide-angle illumination.
- Plesko does not teach or suggest wide-angle illumination at all. This is illustrated in Fig. 2 which shows that in order to illuminate the entire bar-code the hand-held scanner has to be moved along the path Y (see also col. 16, l. 15-22).

Conclusion: A combination of Alcock and Plesko does not render obvious the present invention

a) In applicant's opinion, the present invention is not rendered obvious by a combination of Alcock and Plesko alone for the reason that neither Alcock nor Plesko teaches or suggests wide-angle illumination of a security marking. This has been shown above in great detail.

According to MPEP, §2143,A, in order to find for a case of prima facie obviousness, Office personnel must articulate inter alia the following:

"(1) a finding that the prior art included each element claimed, although not necessarily in a single prior art reference, with the only difference between the claimed invention and the prior art being the lack of actual combination of the elements in a single prior art reference."

In the present case, the prior art consisting of Alcock and Plesko does not include each element claimed. Applicant respectfully submits that there is no case of prima facie obviousness based on a combination of Alcock and Plesko.

b) Moreover, the elements in combination do not merely perform the function that each element performs separately, as required by MPEP, §2143, A:

"(2) a finding that one of ordinary skill in the art could have combined the elements as claimed by known methods, and that in combination, each element merely performs the same function as it does separately".

As shown above, in Plesko the CPC does not function as a wide-angle illuminator. It is used in a completely opposite manner. If one combined the scan-module of Plesko (which includes the CPC) with the device of Alcock, one would not arrive at the present invention unless one re-engineered the device. Then, however, the CPC would not perform any longer the same function as it does separately in the scan-module of Plesko.

"A rationale to support a conclusion that a claim would have been obvious is that all the claimed elements were known in the prior art and one skilled in the art could have combined the elements as claimed by known methods with no change in their respective functions, and the combination would have yielded nothing more than predictable results to one of ordinary skill in the art. *KSR International Co. v. Teleflex Inc*" (MPEP 2143.02).

Applicant respectfully submits that this is not the case here.

c) Applicant also submits that a combination of Alcock with Plesko would not amount to an improvement of a similar device in the device (MPEP, §2143, C). Rather, in order to arrive at the present invention, one would have to use the CPC described in Plesko in a different way.

d) Finally, applicant cannot see any motivation in Alcock or Plesko to modify their teachings in order to arrive at the present invention (MPEP, §2143.01). As noted above, both Alcock and Plesko fail to teach or suggest wide-angle illumination at all. Those prior art references would not have given the skilled person any motivation to make the invention now claimed.

For the reasons expressed above, we earnestly believe the claims now presented are patentable over the prior art of record, and that this application is now in condition for allowance.

Respectfully submitted,

/Charles Fallow/

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September 5, 2008

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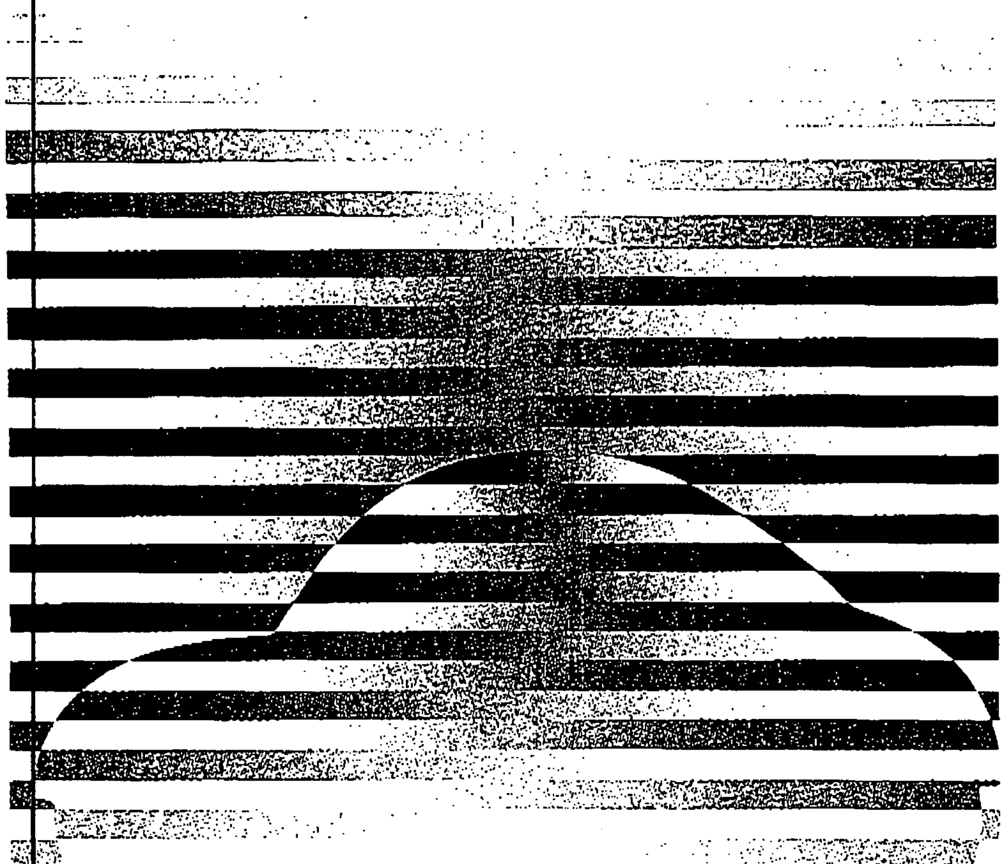
Luster pigments with optically variable properties



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published in
European Coatings
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7-8/97

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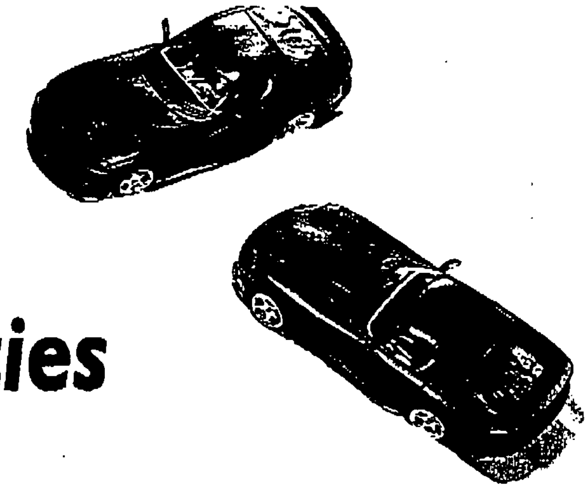
Luster pigments with optically variable properties



Raimund Schmid
Norbert Mronga
Volker Radtke
Oliver Seeger

Luster pigments show angle-dependent color and lightness effects which are based on reflection, interference and absorption phenomena of visible light in pigmentary multilayer systems. New effect pigments which contain combinations of transparent, low refractive layers and highly reflective, absorbing materials will be presented. These pigments exhibit an angle-dependent play of violet, red, gold and green color hues.

Introduction: Interaction of effect pigments with light

The optical impression of plate-like pigments is created by three kinds of interaction with light (*Figure 1*). The first is the directed reflection of incident light, which results in the lightness flop of metallic paint compositions based on aluminum flakes with diameters of more than five microns. Second, if the plate-like particles contain selectively absorbing materials, both the reflected light and the transmitted light are colored. For example, plate-like iron oxides or iron oxide-coated mica pigments exhibit a golden, copper or red reflection color. The third well-known interaction is the interference phenomenon observed in thin films with a thickness in the range of the wavelengths of visible light. The most common example of this type of pigment is TiO_2-coated mica, where the color is determined by the thickness of the TiO_2 coating.

Pigment design of optically variable pigments: soap bubbles as model

Hitherto, the pigment and paint industries have created color with highly absorbing and/or highly refracting materials. In general, the color of a pigment is a function of the absorption constant, refractive index and particle size. The optical impression of plate-like pigments with diameters of more than five microns can be described by the Fresnel equations, wherein the reflection R is a function of the optical constants n (refractive index) and k (absorption) of the materials, the wavelength λ of incident light and the irradiation angle α.

$$R = f(n, k, \lambda, \alpha)$$

In a simplified form ($\alpha = 90°$, $k = 0$ non-absorbing material) the Fresnel equation is

$$R = \left[\frac{n_1 - n_0}{n_1 + n_0}\right]^2$$

This equation clearly shows why the pigment industry prefers highly refractive for obtaining strong gloss effects: the greater the difference between the refractive indices of the plate-like pigment (n_1) and the binder (n_0), the greater is the reflection and, accordingly, the gloss of the pigment.

Common pigments are plate-like bismuthoxychloride crystals and titanium oxide-coated micas. At a geometrical TiO_2 thickness of 40–130 nm the latter show beautiful interference colors, which disappear at steeper angles of view. So the angle-dependent color play is restricted to one interference color hue which disappears at grazing angles. In combination with absorption pigments two-tone effects can be achieved if the absorption color differs from the interference color.

A real color play with various merging interference colors can be seen in soap bubbles. The curved surfaces show strongly angle-dependent color hues e.g. blue-violet-red-gold. The same optical behavior is observed in thin films of inorganic materials such as silicon oxide or magnesium fluoride, which are more suitable in pigment chemistry. In contrast to titanium oxide, soap bubbles and also SiO_2 or MgF_2 are materials with low refractive indices. In the patent literature the low refractive layers are often called dielectric materials, because many dielectrics are non-absorbing and low refracting. Why the interference colors of such materials are highly angle-dependent can be explained by Snell's Law (*Figure 2*).

Snell's Law correlates the refractive angles and the refractive indices. *Figure 2* shows two layers through which light rays pass at a face angle and grazing angle. In the case of TiO_2, both rays are refracted close to the perpendicular. In the case of SiO_2, bending of the rays to the perpendicular is low and therefore the difference between the pathlength of both rays is high. As a result, the interference conditions for face angle rays and for grazing angle rays are completely different and strongly angle-dependent colors are obtained.

Based on this principle one of the best materials for optically variable pigments would be plate-like silicon oxide. However there is one problem: the reflection of SiO_2 surfaces, just as with soap bubbles in air, is weak. It can be calculated from Fresnel's (simplified) equation:

$$R = \left[\frac{n_1 - n_0}{n_1 + n_0}\right]^2 = \left[\frac{1.5 - 1}{1.5 + 1}\right]^2 = \frac{0.25}{6.25} = 0.04$$

(n_1 = refractive index SiO_2, n_0 = refractive index air)

Only 4% of the incident light is reflected and therefore the colors of such materials are weak. More-

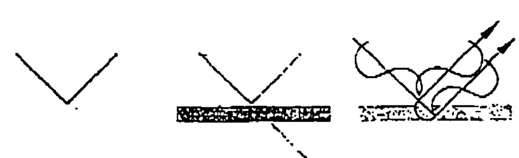


Figure 1: Luster pigments – interaction with light

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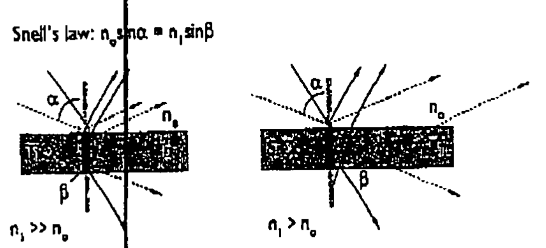

Figure 2: Highly angle-dependent interference colours – Snell's Law

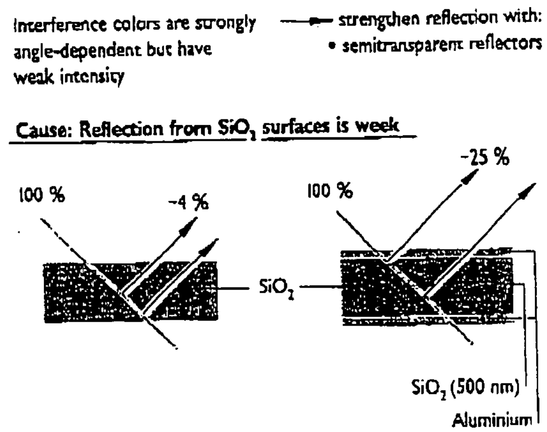

Figure 3: Reflection amplification of SiO_2-films

over, the low refractive material cannot be seen in a binder with a similar refractive index. For this reason, the layer which creates angle-dependent interference colors must be combined with semi-transparent, highly-reflecting layers (*Figure 3*). Therefore the SiO_2 layer is surrounded by reflective materials which strengthen the reflection and thus the chroma of the interference system.

The simplest optical device of this kind has been known since 1897. It is called the Fabry Pérot interferometer and was used to determine the wavelength of light: two semi-transparent metal layers were separated by a layer of air. Using the Fabry-Pérot principle, the structure of the first optically variable pigments[1] was disclosed by Du Pont in 1969 (*Figure 4*): two semi-transparent layers of 5 nm thick aluminium enhanced the reflection of optically variable silicone oxide layers.

The Al-layers are only 5–10 nm thick and therefore the pigments are semi-transparent. Thicker layers of aluminum give better hiding power, but the pigment gets more and more metallic, while the optically variable effect disappears.

A second type of optically variable pigment exists. This type has a core of reflecting material which is surrounded by a symmetrical system of weakly refracting and highly reflecting layers (*Figure 5*).

The systems number 4–7 have opaque metallic cores which are totally reflecting. The other systems contain oxidic and therefore partially reflecting cores. The outer reflecting layer can be varied of a metallic or non-metallic nature. They are all partially reflective; however, there are some important differences concerning n and k. Depending on the different materials, the reflection of light is more or less wavelength-dependent. Therefore, metallic reflectors (Al, Cr, Mo) can be considered to be semi-transparent for all wavelengths, while iron oxide exhibits a selective reflection toward red and yellow light. These differences lead to totally different optical properties.

Coloristic properties of the $Al/SiO_2/Fe_2O_3$ system

The whole color play of optically variable systems cannot be seen with the usual down flop movement

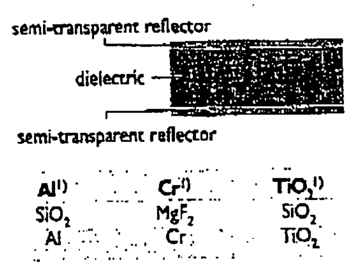

Figure 4: Optically variable pigments of the Fabry-Pérot type

which is used to examine conventional metallic paints. Therefore two extreme illumination and observation positions, face angle and grazing angle (*Figure 6*), are necessary to see all the color shades of the pigments.

At an Fe_2O_3 thickness of approximately 25 nm, several interesting hues occur with increasing SiO_2 thicknesses (*Figure 7*). Due to the selective absorption of iron oxide, golden and red shades have high chroma, while blue shades have weak chroma. At approximately 330–350 nm SiO_2 the $Al/SiO_2/Fe_2O_3$ system exhibits a greenish-gold color, which changes at grazing angle to a reddish-grey with high lightness values. In combination with a blue absorption pigment the greenish-gold color changes to green, while the grazing angle color remains a clear blue. In this way a paint with a green to blue shift can be manufactured. At 370–390 nm SiO_2, the face angle color is red, while the grazing angle color is a greenish-gold.

LIFELINE

Dr. Raimund Schmid, Dr. Norbert Mronga, Dr. Volker Radtke and Dr. Oliver Seeger are all with BASF AG, Ludwigshafen, Germany. It was Dr. Raimund Schmid who presented the paper at the "4th Nürnberg Congress" (Nurnberg, 7-9 April, 1997), which was jointly organized by the Paint Research Association, Teddington, UK and Vincentz Verlag, Hannover, Germany.

Increasing the SiO_2 layer to 460 nm causes a dramatic loss of chroma. This is because this thickness results in a blue interference color, but the color is weakened as a result of the selective absorption of iron oxide. When this pigment is viewed at face angle, only a weak copper shade can be seen. Changing to grazing angle yields an intensive red.

The angle dependent color travel of the OV Pigment red-gold through the CIELAB system is shown in *Figure 8*. The coloristic measurements require both a variation of illumination and observation angle. The beginning of the curves in the red region corresponds to the face angle position, the shift to the yellow region is observed while changing into the grazing angle position.

Coloristic properties of multiple coated, micaceous iron oxides

Replacement of the aluminum core by plate-like iron oxide yields OV pigments which consist simply of layers of iron oxide and silicon oxide (*Figure 9*).

Figure 10 shows the angle-dependent coloristic properties of some $Fe_2O_3/SiO_2/Fe_2O_3$ pigments with different SiO_2 layer thicknesses. As in the aluminum-based OV System, red and gold hues have strong chroma values, while blue shades are weak.

Figure 11 shows the coloristic properties of paints based on OV pigment red-gold in combination with conventional absorption pigments.

Classical synthesis: Physical Vapor Deposition (PVD)

The first synthesis of optically variable pigments was described in 1969. In a vacuum chamber, vapors of aluminum and silicon oxide were created by heating and then deposited on a plane surface. After the coating steps, the vacuum chamber was opened and the layers were scratched off the substrate and broken down to pigment size. The resulting flakes were extremely smooth and showed brilliant angle-dependent colors. But due to the complicated process, only small quantities could be manufactured. 15 years later advanced PVD technologies (roil coaters, sputtering techniques) enabled larger surfaces to be coated. Several tons of pigments p.a. can be manufactured by this method.

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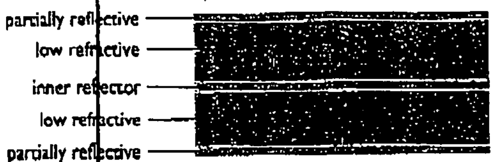


Al[4]	Cr[5]	MoS_2[6]	Fe_2O_3[7]	Fe_2O_3[8]	MoS_2[9]	Fe_2O_3[10]
SiO_2	MgF_2	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2
Al	Al	Al	Al	Fe_2O_3	mica/oxide	mica/oxide
SiO_2	MgF_2	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2
Al	Al	MoS_2	Fe_2O_3	Fe_2O_3	MoS_2	Fe_2O_3

Figure 5: Optically variable pigments with inner reflector

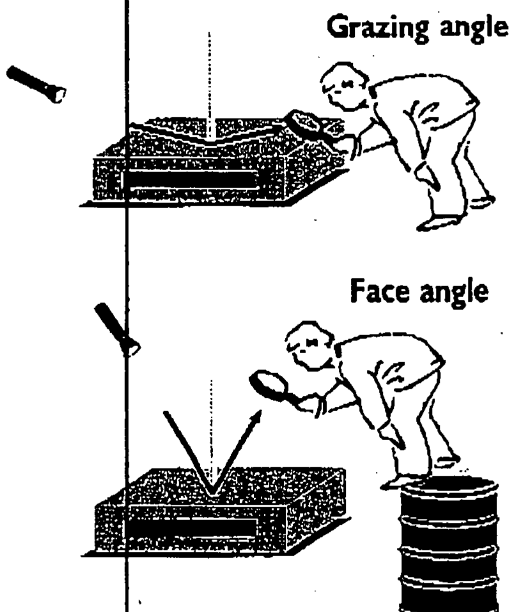
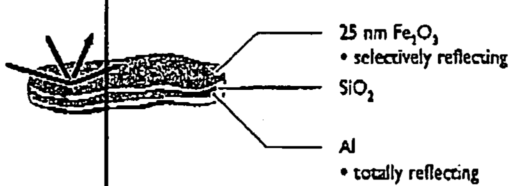


Figure 6: Two extreme illumination and observation positions – grazing angle and face angle



SiO_2 thickness	face angle color	grazing angle color
320 – 350 nm	greenish gold	reddish grey
380 – 400 nm	red	gold
410 – 420 nm	violet	green
430 – 440 nm	weak copper	red

Figure 7: Colour hues in the $Al/SiO_2/Fe_2O_3$ system

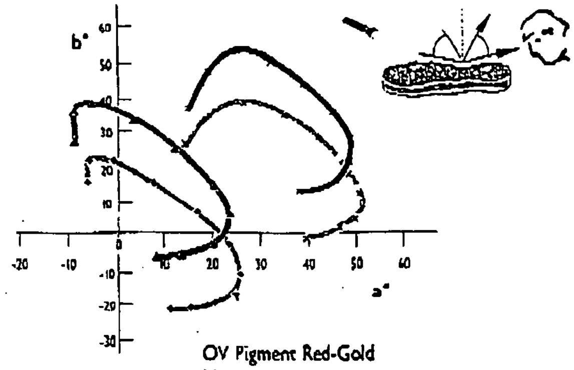


Figure 8: Angle-dependent colour travel of $Al/SiO_2/Fe_2O_3$ pigments (CIELAB); OV pigment Red-Gold combined with absorption pigments

New synthesis: successive coatings of plate-like particles chemically

The chemical synthesis of optically variable pigments with central reflecting cores began in 1991. Several different systems with interesting optical properties have been developed. The principle of the chemical syntheses is to coat commercially available, plate-like pigments with a low refractive layer and in a further step with a semi-transparent, reflecting film. The chemical coating methods are of the wet chemical type or of the chemical vapor deposition (CVD)-type (*Figure 12*).

First step:
Coating of flakes with a low refractive layer

The flakes are suspended in an alcohol with dispersion aids. Tetraethoxysilane and an aqueous solution of ammonia is continuously added to this solution. Under these conditions, tetraethoxysilane is hydrolyzed and the resulting hydrolysis product, the hypothetical silicic acid $Si(OH)_4$, condenses and forms SiO_2 as a smooth film on the substrates. Depending on the specific surface of the substrates, 25–80% of silicon oxide is necessary to obtain optically variable effects. Alternatively the SiO_2-coating can also be carried out in a fluidized-bed reactor. In this case vapors of tetraethoxysilane must react with water vapor. However, at the preferred temperatures of the gas-phase deposition (100–300 °C), tetraethoxysilane does not react in satisfactory yields. For this reason special precursors, which are more reactive have to be used. Suitable precursors are of the $Si(OR)_2(OOCR)_2$-type. They vaporize at 150 °C and decompose easily with water at 200 °C.

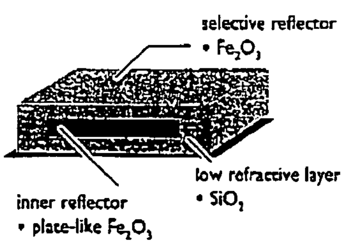


Figure 9: OV pigments based on plate-like iron oxide

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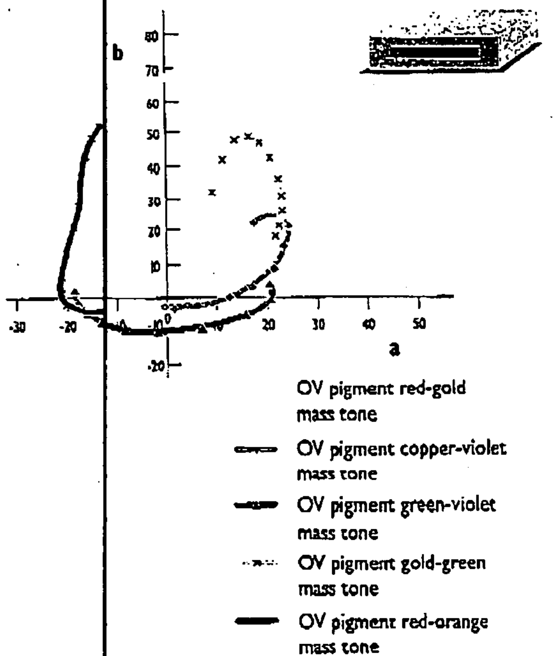

Figure 10: Angle-dependent colour travel of multiple coated, micaceous iron oxides (CIELAB), various pigments (1)

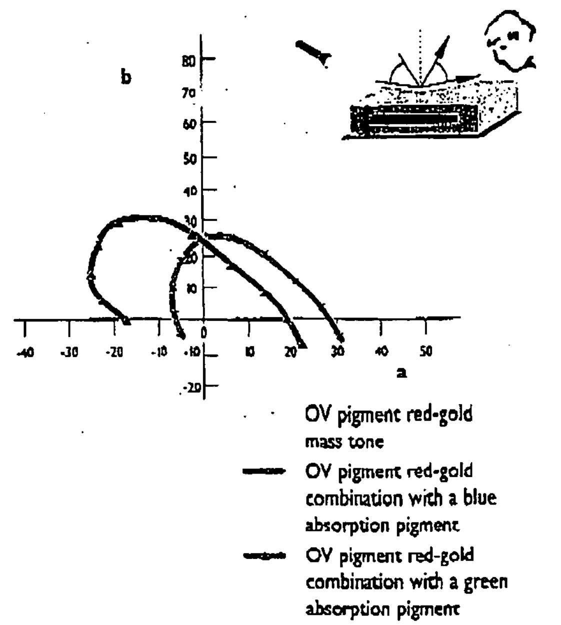

Figure 11: Angle-dependent colour travel of multiple coated, micaceous iron oxides (CIELAB), various pigments (2)

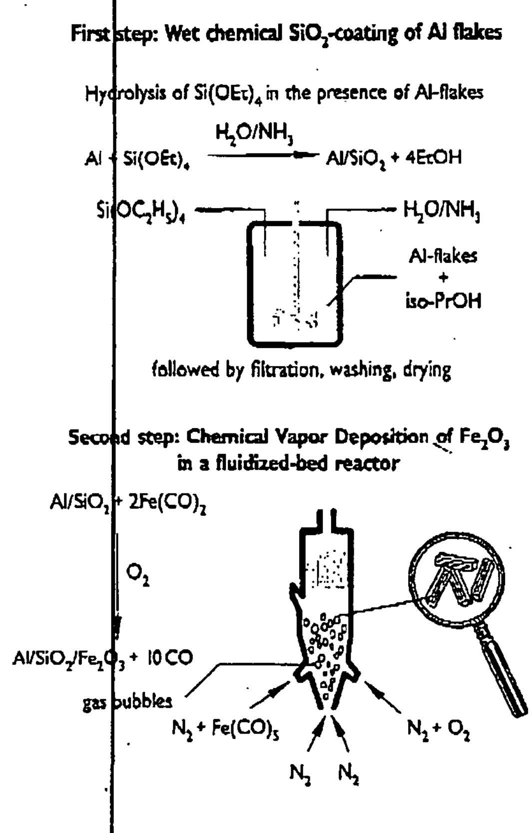

Figure 12: Chemical synthesis of OV pigments

Second step:
Coating of the flakes with the reflecting layer

In a chemical vapor deposition process the silicon oxide-coated pigments are coated with metal oxides or metal films. The coating takes place in a fluidized-bed reactor. The pigments are fluidized with inert gases, which are charged with gaseous metal carbonyls. At 200 °C the carbonyls decompose. If iron carbonyl is used, it can be oxidized to Fe_2O_3, which forms smooth thin films on the pigment surfaces.

$$Al/SiO_2 + 2\,Fe(CO)_5 + 3/2\,O_2 \rightarrow Al/SiO_2/Fe_2O_3 + 10\,CO$$

As an alternative method the iron oxide coating can be carried out in a sol-gel technique known from conventional micas.

When the carbonyls of chromium, molybdenum or tungsten are decomposed under inert conditions, metallic films can be obtained:

$$Al/SiO_2 + Cr(CO)_6 \rightarrow Al/SiO_2/Cr + 6\,CO$$
$$Al/SiO_2 + Mo(CO)_6 \rightarrow Al/SiO_2/Mo + 6\,CO$$

The Mo films are not stable against water attack and they are therefore converted to molybdenum sulfide. The dry pigments are mixed with sulfur powder and the mixture is heated under inert conditions to 500 °C. Under these conditions, the sulfur vaporizes and reacts with the Mo layer:

$$Al/SiO_2/Mo + 2\,S \rightarrow Al/SiO_2/MoS_2$$

Summary

The coating of plate-like, reflecting pigments with weakly refracting, non-absorbing layers and semi-transparent iron oxide films lead to optically variable pigments with color flops in the red, golden and green color space. The combination with absorption pigments leads to new vivid colors with exciting, angle-dependent hues. The new optically variable pigments are useful for many purposes, such as coloring plastics, glass, ceramic products, decorative cosmetic preparations and coatings, especially automotive coatings and printing inks.

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